OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT N00014-95-1-1183

SIMULATIONS OF TRIBO~~LOGY~~ chemistry AT CARBON/METAL INTERFACES

by

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END-OF-YEAR REPORT (Part I)
Grant # N00014-95-1-1183

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a. *Papers submitted to refereed journals (not yet in print):*

- "Simulated Engineering of Nanostructures", D. W. Brenner, S. B. Sinnott, J. A. Harrison and O. A. Shenderova, *Nanotechnology*, 1996, submitted for publication.

b. *Papers published in refereed journal:* None.

c. *Books (and chapters thereof) submitted (not yet in print):* None.

d. *Books (and chapters thereof) published:*

- "Molecular Dynamics Simulation of Atomic-Scale Adhesion, Deformation, Friction, and Modification of Diamond Surfaces", J.A. Harrison, S.B. Sinnott, C.T. White, D.W. Brenner and R.J. Colton, H.-J. Guentherodt et al. (Eds.), *Forces in Scanning Probe Methods*, Kluwer Academic Publishers, The Netherlands, 1995, pp.175-181.

e. *Technical reports and non-refereed papers published:* None.

f. *Patents files:* None.

g. *Patents granted:* None.

h. *Invited presentations at workshops or professional society meetings:* None.

I. Presentations at workshops or professional society meetings:

- "Molecular Dynamics Investigations of the Nanometer-Scale Indentation of Amorphous Carbon Thin Films", S. B. Sinnott, C. T. White, R. J. Colton, D. W. Brenner and J. A. Harrison, Sixth Conference on Computational Research on Materials, Morgantown, WV, May 8-10, 1996.

j. Honors/Awards/Prizes:

- Oak Ridge Associated Universities Junior Faculty Enhancement Award, 1996.
- Co-Finalist for the Foresight Institute Feynman Prize in Nanotechnology, 1995.

k. Number of graduate students and postdoctoral associates supported by this grant: None.

l. Other funding:

- University of Kentucky - Research Committee Grant, "Grain Boundary Effects on Material Yield", PI: S. B. Sinnott, $4,846, 10/1/96 - 1/27/97.
- Oak Ridge National Laboratory Junior Faculty Enhancement Award Program, "Computational Approaches To Nanometer-Scale Engineering", PI: S. B. Sinnott, $10,000, 4/1/96-3/31/97.

END-OF-YEAR REPORT (Part II)
Grant # N00014-95-1-1183

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d. *Brief description of project:*

The goal of the project is to gain increased understanding of the atomic-scale chemical interactions responsible for macroscopic friction and wear when two surfaces are brought into sliding contact with each other. Such insight is crucial to the development of improved solid-state lubricants and, consequently, improved machines of technological and military importance. The approach is molecular dynamics simulations to provide detailed information about the tribochemistry that occurs when films of carbon solid-state lubricants, such as graphite and diamond-like carbon, are placed between metal surfaces in sliding contact with each other. To facilitate realistic interactions between the carbon and metal atoms, a combined many-body carbon -metal (MBCM) potential must be constructed that allows one to realistically characterize systems composed of thousands of carbon and metal atoms on a standard workstation.

e. *Significant results during last year:*

A combined many-body carbon-metal (MBCM) potential suitable for use in large-scale atomistic simulations has been constructed. The combined potential reduces to the reactive empirical bond order (REBO) form of Brenner et al. for carbon-carbon and carbon-hydrogen interactions, and to the corrected effective-medium (CEM) form for metal-metal interactions. The metal-carbon interactions are characterized by an expression of the effective-medium type:

$$E_{Cohesive} = \sum_i [\Delta F(n_i) + \frac{1}{2} \sum_{j \neq i} \Theta(r_{ij})] \quad (1)$$

where Θ is a pair additive term that accounts for the attractive core-electron interactions, and ΔF is the energy of "embedding" each into jellium of density n_i (i.e., the energy difference between the atom-in-jellium system and the isolated atom and jellium systems). The jellium density is obtained from the sum of the overlaps of the atomic densities.

The first systems to be examined as test cases are CH_x (x=0-3) chemisorbed on nickel surfaces. These systems were chosen because 1) when a metal surface is in sliding contact with a carbon lubricant, it is expected that parts of the lubricant will be transferred to the metal surface; 2) there is ample first principles data available with which to compare the test results; and 3) nickel substrates are used to grow diamond films by chemical vapor deposition techniques, a process that could be studied in molecular simulations with this potential. Some preliminary results are shown below:

	$r_{c\text{-}Ni}$ (Å)		Cohesive Energy (eV)	
	this work	first principles[a]	this work	first principles[a]
C-Ni diatomic	1.68	1.63[b]	-3.49	-4.93[b]
C/Ni(100) [h]	1.91	1.85[c]	-5.84	-6.51[c]
C/Ni(100) [a]	1.73	-	-2.55	-
CH/Ni(111) [h]	1.89	2.30	-3.89	-3.00
CH/Ni(111) [b]	1.83	2.36	-2.87	-2.90
CH/Ni(111) [a]	1.72	1.74	-1.54	-1.69
CH_2/Ni(111) [h]	1.89	2.31	-2.85	-2.80
CH_2/Ni(111) [b]	1.83	2.29	-1.82	-2.72
CH_2/Ni(111) [a]	1.73	2.36	-0.50	-1.58
CH_3/Ni(111) [h]	1.89	2.59	-2.76	-1.68
CH_3/Ni(111) [b]	1.83	2.65	-1.73	-1.54
CH_3/Ni(111) [a]	1.73	2.03	-0.40	-1.47

[a] From H. Yang and J. L. Whitten, Surf. Sci. **255**, 193 (1991) unless otherwise indicated.

[b] First principles LDA calculations from B. I. Dunlap (private communication)

[c] From P. E. M. Siegbahn and I. Panas, Surf. Sci. **240**, 37 (1990).

[h]=hollow site; [b]=bridge site; [a]=atop site

The table shows that the MBCM potential is in good qualitative agreement with available first principles data. Most of the trends are captured correctly, and the potential could be used to study the *general* tribochemistry of a metallic material interacting with a covalently bonded material. It is also expected that the potential will open up to large scale computing many other important problems in materials and surface science, such as corrosion and heterogeneous catalysis. However, some refining will be necessary to obtain improved quantitative agreement with the first principles data and to allow charge transfer between the atoms.

f. Summary of plans for FY 96-97

Plans for FY 96-97 will be to refine the MBCM potential to improve the agreement with the first principles data The first task will be to construct a new embedding energy fit for carbon (the first term in Eq. (1)). This is currently fit to carbon-carbon molecular and solid-state data. A new fit to first principles data for carbon-nickel interactions will lead to an improved characterization of the carbon-metal bonds at various electron density overlaps. The second task will be to optimize the bond angles for carbon-carbon bonds when one of the carbon atoms is connected to a metal atom. The data to fit these angles will also be obtained from first principles calculations.

Finally, because the chemical bonding will change drastically in the course of the simulations, a way of determining environment-dependant partial atomic charges and charge transfer will be necessary. A formalism recently introduced for describing electrostatic forces in alumina will be adapted and incorporated into the MBCM expression. This is an approach that determines the net charges on each atom from an environment-dependant electronegativity term, which is calculated from the atomic electron densities associated with each atom. These atomic electronegativites will be fit to reproduce the partial charges on the atoms predicted from first principles calculations.

g. Graduate students and postdoctoral associates associated with the project:

At the moment, the PI's group consists of one PhD graduate student, Mr. Lifeng Qi, and one Masters graduate student, Mr. Matthew Flanagan. It is expected that Mr. Qi will be heavily associated with the above project in the course of completing his PhD under the direction of the PI.

END-OF-YEAR REPORT (Part III)
Grant # N00014-95-1-1183

Explanatory material for view graph information

Energies and Configurations of Hydrocarbons Adsorbed on Ni(100) and Ni(111)

A combined many-body carbon-metal (MBCM) potential suitable for use in large-scale atomistic simulations has been constructed. The combined potential reduces to the reactive empirical bond order (REBO) form of Brenner et al. for carbon-carbon and carbon-hydrogen interactions, and to the corrected effective-medium (CEM) form for metal-metal interactions. The metal-carbon interactions are characterized by an expression of the effective-medium type. The motivation behind the construction of the potential is to examine and characterize the atomic-scale phenomena responsible for the macroscopically observed friction and wear of metal surfaces in sliding contact with each other and the role of carbon-based solid lubricants in this process.

The view graph shows preliminary test results of sample systems of CH_x (x=0-3) chemisorbed on nickel surfaces. These systems were chosen because 1) when a metal surface is in sliding contact with a carbon lubricant, it is expected that parts of the lubricant will be transferred to the metal surface; 2) there is ample first principles data available with which to compare the test results; and 3) nickel substrates are used to grow diamond films by chemical vapor deposition techniques, a process that could be studied in molecular simulations with this potential.

The first principles data was obtained from the following sources:

- CH_x/Ni(111) (x=1-3) from Yang and Whitten, Surf. Sci. **255**, 193 (1991)
- carbon-nickel diatomic from B. I. Dunlap (private communication)
- C/Ni(100) from Siegbhn and Panas, Surf. Sci. **240**, 37 (1990).

Results From Realistic Empirical Carbon-Metal Potential
CH_x (x=0-3) Chemisorbed on Ni(100) and Ni(111)

	$r_{c\text{-}Ni}$ (Å)		Cohesive Energy (eV)	
	this work	first principles	this work	first principles
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The goal of the project is to gain increased understanding of the atomic-scale chemical interactions responsible for macroscopic friction and wear when two surfaces are brought into sliding contact with each other. Such insight is crucial to the development of improved solid-state lubricants. The approach is molecular simulations to provide detailed information about the tribochemistry that occurs when films of carbon solid lubricants are placed between metals surfaces in sliding contact. To facilitate realistic interactions between the carbon and metal atoms, a combined many-body carbon-metal potential has beenconstr-ucted that allows for the characterize systems composed of thousands of carbon and metal atoms on a standard workstation. Testing of the potential has yielded very promising results with some room for improvment.

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